Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information for: "On the Application of Marcus-Hush Theory to Small Polaron Chemical Dynamics in Oxides: Its Relationship to the Holstein Model and the Importance of Lattice-Orbital Symmetries"

Zi Wang, Bobby Miglani, and Shuaishuai Yuan
Division of Materials Engineering, Faculty of Engineering, McGill University, Montréal, Québec, Canada.

Kirk H. Bevan
Division of Materials Engineering, Faculty of Engineering, McGill University, Montréal, Québec, Canada and Centre for the Physics of Materials, McGill University, Montréal, Québec, Canada

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A. Fully Trapped Polarons

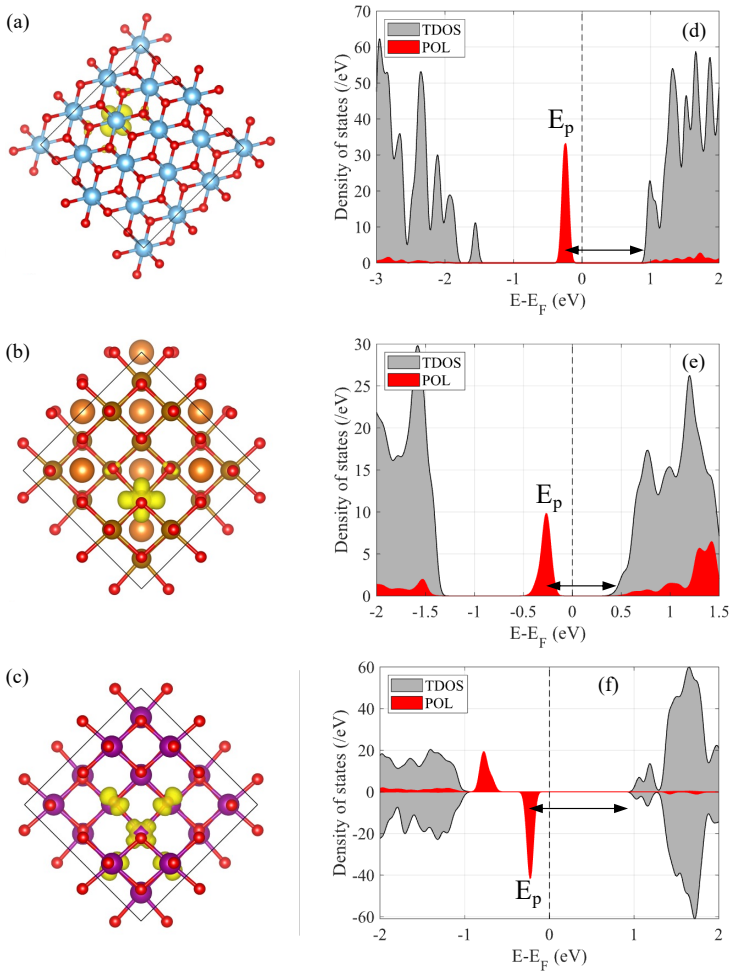

FIG. S1. (a-c) Well localized charge density profiles for fully trapped electron polarons in their ground state of TiO_2, $MgFe_2O_4$, and Mn_2O_4. Isocharge surfaces were respectively plotted at 0.0052 e/Å^3, 0.0056 e/Å^3, and 0.0036 e/Å^3. (d-f) Density of states (DOS) plots showing a fully trapped polaron state (at E_p) well below the conduction band minimum of their respective material. The projected DOS (PDOS) of the d-orbitals on the trapping cation site is shown in red and the total DOS (TDOS) is shown in grey. Mn_2O_4 shows some additionally delocalization in the fully trapped state due to p-orbital hybridization, but less so than at the transition state as shown in the main manuscript.

B. Total Energy Fits

The 1D Holstein tight-binding model was fitted to match the ratios $E_a/(\varepsilon_+ - \varepsilon_-)$ and $(\varepsilon_c - \varepsilon_+)/(\varepsilon_+ - \varepsilon_-)$ at the transition state ($\bar{x} = 0$) for each respective material calculation in the main manuscript. In the case of TiO_2 2L hopping, where the excited state is pushed into the conduction band, only the first parameter was fitted. The resulting fits are meant to be qualitatively expressive of the general physical trends and not quantitative.

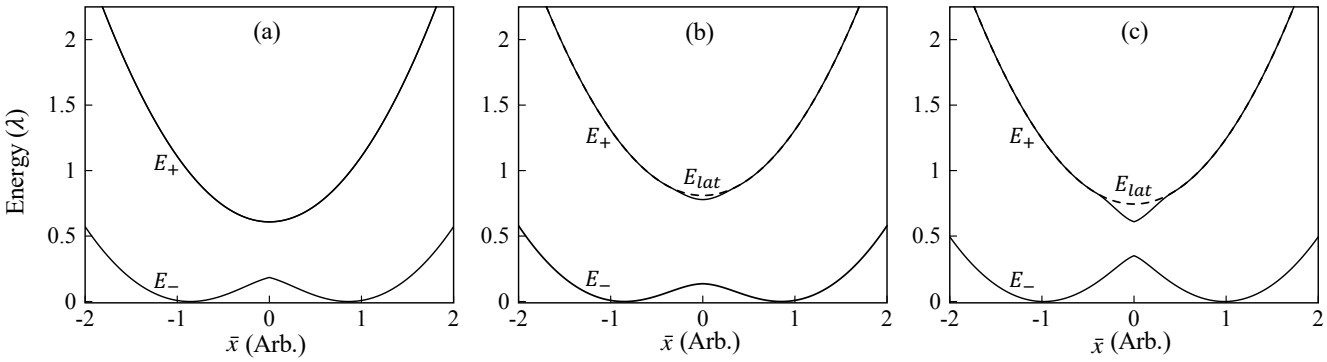

FIG. S2. Hostein 1D model total energy fits for three of the hopping cases studied in the manuscript. (a) TiO_2 hopping fit in the 2L direction. (b) $MgFe_2O_4$ hopping fit. (c) $Mn2O_4$ hopping fit. The corresponding single-particle energy and wavefunction plots can be found in the main manuscript.

C. Model Codes

Codes for the model calculations employed in this study can be found here:
`http://www.physics.mcgill.ca/~bevankh/Codes/MarcusHolsteinPolaron2023.zip`